

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

Chains, Rings and Spectroscopy

2814

Friday

21 JANUARY 2005

Morning

1 hour 30 minutes

Candidates answer on the question paper.

Additional materials:

Data Sheet for Chemistry

Scientific calculator

Candidate Name

Centre Number

Candidate
Number

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TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

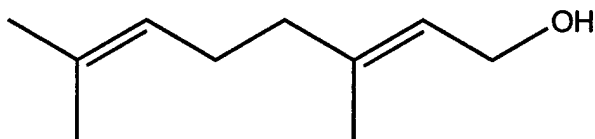
FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	20	
2	17	
3	13	
4	16	
5	10	
6	14	
TOTAL	90	

This question paper consists of 15 printed pages and 1 blank page.

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Answer **all** the questions.

- 1 Geraniol, $C_9H_{15}CH_2OH$, is a naturally occurring compound that contributes to the smell of roses. The skeletal formula of geraniol is shown below.



geraniol

- (a) Name the two different functional groups in geraniol.

..... and [1]

- (b) Geraniol has stereoisomers due to one of the double bonds in the molecule.

- (i) What is meant the term *stereoisomer*?

.....

 [1]

- (ii) Name the type of stereoisomerism shown by geraniol.

..... [1]

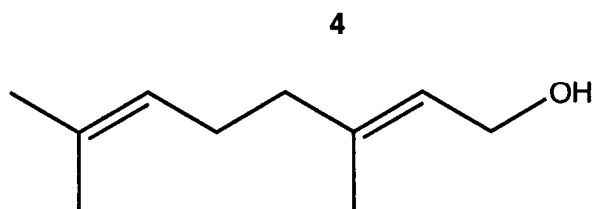
- (iii) State how this type of stereoisomerism arises in organic molecules.

.....
 [1]

- (iv) Explain why one of the double bonds in geraniol does **not** give rise to stereoisomerism.

.....

 [1]



geraniol

(c) Mild oxidation of geraniol gives an aldehyde **Y**.

(i) Draw the skeletal formula of aldehyde **Y** below.



aldehyde **Y**

[2]

(ii) Complete the equation for the oxidation of geraniol to aldehyde **Y**.



[2]

(d) Reaction of geraniol with ethanoic acid can be used to make ester **Z**, which is used in chewing gum and desserts.

(i) Suggest why esters are used in the manufacture of foods.

.....[1]

(ii) State the conditions needed to make ester **Z** from geraniol and ethanoic acid.

.....
.....[2]

(iii) Complete the equation for the formation of ester **Z**.



[3]

- (e) Infra-red spectroscopy can be used to distinguish between geraniol, aldehyde **Y** and ester **Z**.

Describe how the infra-red spectra of these three compounds differ. Identify the wavenumber ranges at which you would expect to find the characteristic absorptions for each of the three compounds.

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[5]

[Total: 20]

2 The nitration of benzene is a very important industrial reaction.

- (a) Name **two** types of commercially important material whose manufacture involves the nitration of benzene.

.....
[2]

- (b) State the conditions required for the nitration of benzene using nitric acid and sulphuric acid.

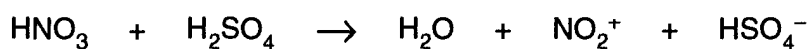
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[2]

- (c) Write a balanced equation for the nitration of benzene.

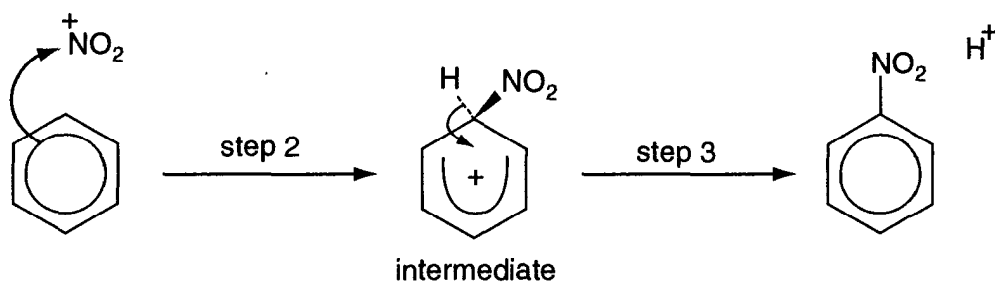
[2]

- (d) The mechanism for the reaction is given below.

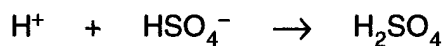
Step 1: formation of the electrophile, NO_2^+ , from HNO_3 and H_2SO_4



Steps 2 and 3: substitution of NO_2^+ into the benzene ring



Step 4: protonation of the HSO_4^-



- (i) Explain what a curly arrow  represents in this type of mechanism.

.....
[2]

(ii) State why the NO_2^+ is described as an electrophile in this mechanism.

.....
[1]

(iii) State why this mechanism is described as substitution.

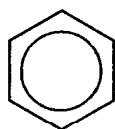
.....[1]

(iv) How does the mechanism show that the sulphuric acid is acting as a catalyst?

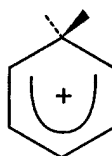
.....
[1]

(e) In this question, one mark is available for the quality of spelling, punctuation and grammar.

The benzene ring and the ring in the intermediate formed after **step 2** have different structures shown below. Both structures have π -bonds.



benzene ring



ring in the intermediate

Deduce how many electrons are involved in the π -bonding in each structure and describe how their arrangements are different.

.....

[5]

Quality of Written Communication [1]

[Total: 17]

[Turn over

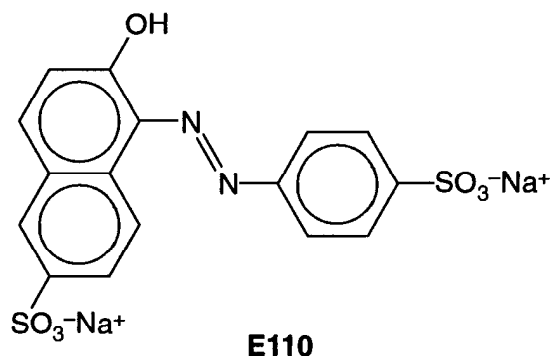
E110 contains an azo dye made from an amine and a phenol.

Include in your answer

- essential reagents and conditions for each stage
- names of any functional groups formed during the process.

.....[7

(b) The structure of E110 is shown below.



(i) On the structure above, draw a circle around the functional group that identifies this molecule as an azo dye. [1]

(ii) Deduce how many carbon and hydrogen atoms are in a molecule of E110.

..... carbon atoms and hydrogen atoms. [2]

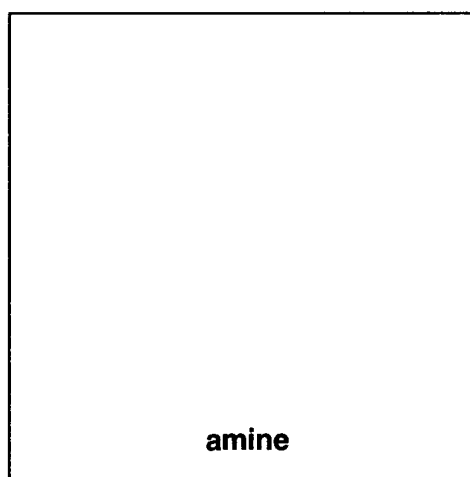
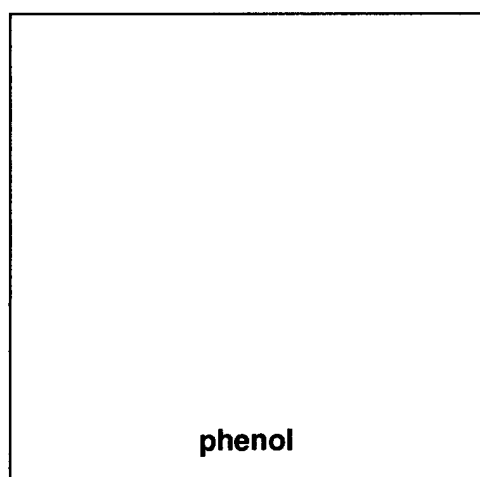
(c) The solubility of E110 in water can be improved by converting the phenolic -OH group into a charged -O^- group.

Suggest a suitable reagent that will convert the -OH group in E110 into an -O^- group.

.....[1]

(d) In the boxes below, draw the structures of a phenol and an amine that could be used to make E110 by the method in part (a).

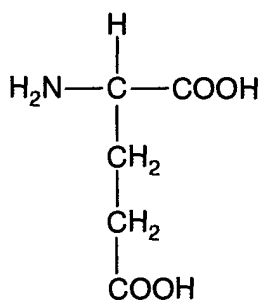
Assume that the $\text{SO}_3^- \text{Na}^+$ groups do not change during the process.



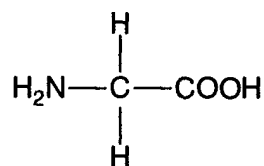
[2]

[Total: 13]

- 4 Glutamic acid and glycine are both α -amino acids that occur widely in living organisms. Their structures are shown below.



glutamic acid



glycine

- (a) (i) State the general formula for an α -amino acid.

.....[1]

- (ii) Explain how glutamic acid and glycine both fit the general formula given in part (i)

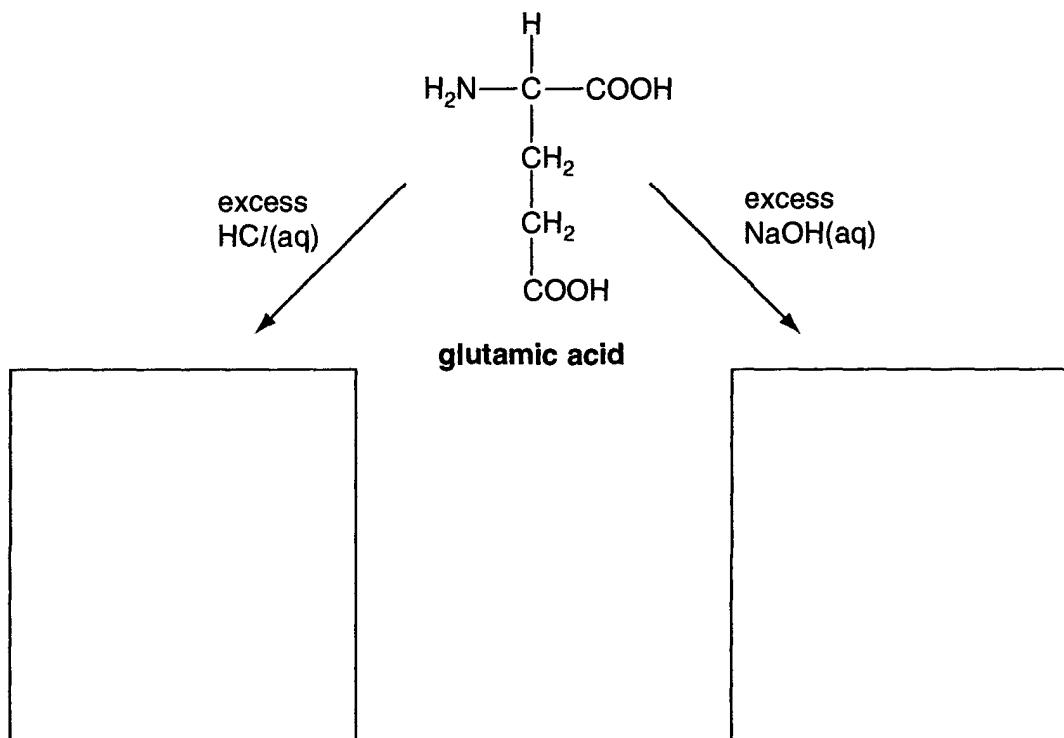
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.....[2]

- (b) Amino acids react with both acids and alkalis.

Draw structures below to show how the glutamic acid molecule is changed in the presence of excess acid and alkali.



[5]

- (c) In this question, one mark is available for the quality of use and organisation of scientific terms.

Glutamic acid exists as two optical isomers, but glycine does not.

Explain what structural feature causes optical isomerism in organic molecules. Include appropriate diagrams and use these two amino acids to illustrate your answer.

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[7]

Quality of Written Communication [1]

[Total: 16]

- 5 Poly(phenylethene) is one of the most versatile and successful polymers.

The 3-D skeletal formula of a section of atactic poly(phenylethene) is shown in **Fig 5.1** below.

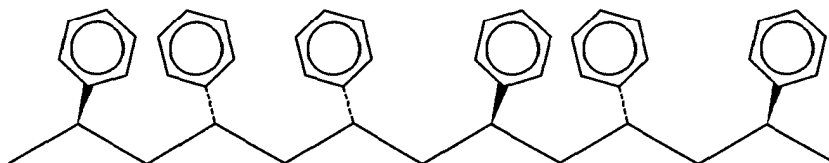


Fig. 5.1

- (a) (i) State the type of polymerisation used to make poly(phenylethene).

.....[1]

- (ii) Draw a skeletal or displayed formula to show the monomer used to make poly(phenylethene).

[1]

- (iii) Outline how the polymer is formed from the monomer molecules. (You do **not** need to give any details of the catalyst or conditions involved.)

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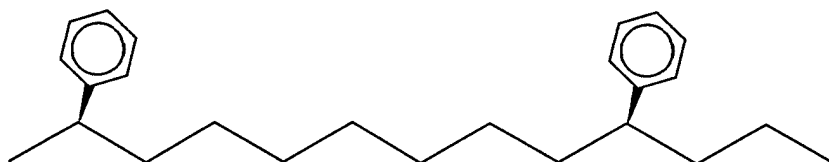
.....

.....[2]

- (b) Poly(phenylethene) can also be made with a *syndiotactic* arrangement of its side chains.

Explain what is meant by the term *syndiotactic*. Illustrate your answer by completing the 3-D skeletal formula of a section of syndiotactic poly(phenylethene) below.

.....



[3]

- (c) Syndiotactic poly(phenylethene) has a high melting point and is particularly useful in situations in which the polymer might get hot.

Suggest why the syndiotactic poly(phenylethene) has a higher melting point than the atactic poly(phenylethene) shown in **Fig. 5.1**.

.....

[3]

[Total: 10]

- 6 Forest fires release a large number of organic compounds into the atmosphere. These include alcohols and carboxylic acids. An environmental chemist is trying to identify one of these compounds in a sample of air.

The unknown compound **X** is thought to be a carboxylic acid with empirical formula $C_2H_3O_2$.

(a) Mass spectrometry is used to help deduce the molecular formula of compound **X**.

- (i) Describe how the mass spectrum of compound **X** is used to determine its relative molecular mass.

.....
[2]

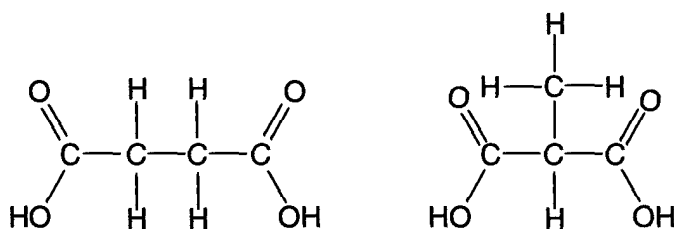
- (ii) The relative molecular mass of compound **X** is shown to be 118.

Explain how this relative molecular mass and the empirical formula are used to deduce that the molecular formula of compound **X** is $C_4H_6O_4$. Show any working.

.....

[2]

(b) The two dicarboxylic acids with molecular formula $C_4H_6O_4$ are shown below.



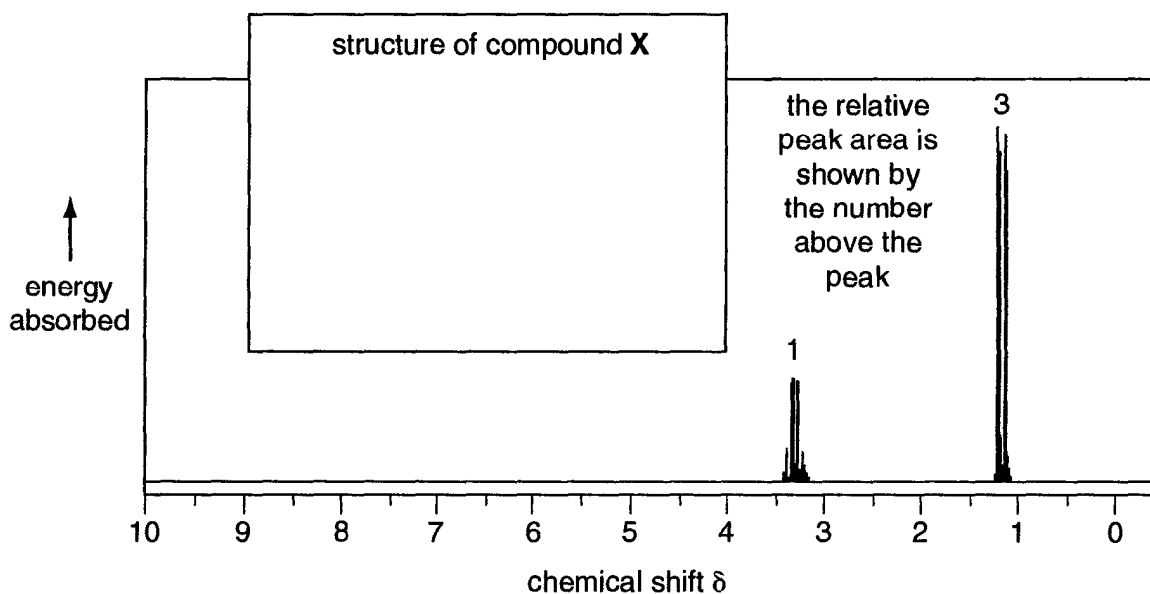
N.m.r. spectroscopy is used to deduce which of these is the unknown compound.

The environmental chemist obtains an n.m.r. spectrum of compound **X** and then adds some D_2O and obtains a second n.m.r. spectrum.

- (i) What difference would you expect between these two n.m.r. spectra?

.....
[1]

(ii) The n.m.r. spectrum of compound **X** in D₂O is shown below.



Use this spectrum to identify which of the two carboxylic acids is compound **X**.

- Draw the correct structure in the box above the spectrum.
- Use labels to show which protons on the structure are responsible for each peak on the spectrum.
- Explain your reasoning by referring to the relative peak areas and the spin-spin splitting patterns of the peaks.

.....[6

TURN OVER FOR Q6 PART (b)(iii)

- Explain your reasoning.**

O=C(C)C(=O)O
O=C1C(=O)C(=O)O1

[3]

[Total: 14]

END OF QUESTION PAPER

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